Revealed Architectures of Adsorbed Polymer Chains at Solid-Polymer Melt Interfaces

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We report the chain conformations of polymer molecules accommodated at the solid-polymer melt interfaces in equilibrium. Polystyrene "Guiselin" brushes (adsorbed layers) with different molecular weights were prepared on Si substrates and characterized by using x-ray and neutron reflectivity. The results are intriguing to show that the adsorbed layers are composed of the two different nanoarchitectures: flattened chains that constitute the inner higher density region of the adsorbed layers and loosely adsorbed polymer chains that form the outer bulklike density region. In addition, we found that the lone flattened chains, which are uncovered by the additional prolonged solvent leaching (~ 120 days), are reversibly densified with increasing temperature up to 150 °C. By generalizing the chain conformations of bulks, we postulate that the change in probabilities of the local chain conformations (i.e., *trans* and *gauche* states) of polymer molecules is the origin of this densification process.

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Solid-polymer melt (SPM) interfaces play crucial roles in a multidisciplinary field of nanotechnology at the confluence of physics, chemistry, biology, and engineering. One of the fundamental but unsolved questions is the equilibrium conformations of polymer chains accommodated at the SPM interfaces. It is known that polymer chains adsorb even onto weakly attractive surfaces [1], forming three types of segment sequences, "trains" (adsorbed segments), "loops" (sequences of free segments connecting successive trains), and "tails" (nonadsorbed chain ends) [2]. The lattice mean-field model by Schuetjens and Fleer [3–5] and lattice Monte Carlo simulations [6] by Bitsanis and ten Brinke led to the strong conclusion that the chain conformational features of homopolymer melts at the SPM interfaces are independent of chain intramolecular architectures, molecular weights, and strength of surface-segment interactions. Unfortunately, the experimental situations to gain the chain statistics of adsorbed polymer chains separately from those of unadsorbed chains still remain challenging. Recently though, several research groups utilized the approach proposed by Guiselin [7] which combines prolonged thermal annealing (to equilibrate the melt against the wall) and subsequent solvent leaching (to remove nonadsorbed chains) [8–15], uncovering the formation of a polymer adsorbed layer (i.e., a "Guiselin" brush) with several nanometers thick on the substrate surfaces. In particular, Durning *et al.* [16] and Fujii *et al.* [10] showed that the thickness of the equilibrated adsorbed layers increased with increasing molecular weights, which is in sharp contrast to the above theoretical prediction. Thus, a molecular scale description of the real chain conformations, currently lacking, is crucial to provide insight into the mechanism of polymer adsorption from the melts and to bridge the gap between the theoretical and experimental viewpoints. Furthermore, since there is now growing evidence that the effects of the adsorbed layers at the SPM interfaces result in the long-range perturbations on various properties of supported polymer thin films [15–18], a better understanding of the chain conformations would also be a key for the development of new polymer nanostructures and nanoscale devices.

In this Letter, by combining *in situ* x-ray reflectivity (XR) and neutron reflectivity (NR), we report the novel nanoscale architectures of adsorbed polymer chains established at the SPM interfaces. Polystyrene (PS) adsorbed layers with different molecular weights were prepared on cleaned silicon (Si) substrates as model systems since the equilibrium layer preparation protocol based on the Guiselin's approach has been well established [10,14]. The results show that the equilibrium PS adsorbed layers have the two different density regions in the direction normal to the surface: the nearly identical inner higher density region regardless of molecular weights and the outer bulklike density region whose thickness increases with increasing molecular weights. Based on the picture developed by Granick and co-workers for polymer adsorption from a dilute solution [19–22], we conjecture that polymer molecules arriving first on the surface are adsorbed with a flat conformation, forming the inner high-density region, while late arriving ones, which find fewer free surface areas and are hence adsorbed more loosely, form the outer bulklike density region. In addition, we found that the further prolonged leaching process (up to 150 days) allows us to preferentially remove the outer bulklike density layer, uncovering the lone flattened higher density layer. Intriguingly, the lone higher density layer is further densified with increasing temperature up to 150 °C, and the phenomenon is reversible as a function of temperature. By generalizing the chain conformations of bulks, we found that this unusual densification process is correlated with the change in the probabilities of the local chain conformations (i.e., *trans* and *gauche* states) of the adsorbed polymer molecules. Our finding suggests that the increase in the flexibility of the chains associated with the increase in the fraction of *gauche* conformers may be the origin of the reversible densification process.

Five different weight-average molar masses (M_w) of PS ($M_w = 123$, 170, 290, 650, and 2000 kDa) with narrow polydispersities ($M_w/M_n = 1.02$–1.05, where M_n is the number-average molar mass) were obtained from Polymer Laboratories Inc. (Amherst, MA) [23]. We reproduced the established protocol for PS adsorbed layers [10,14] on cleaned hydrogen-passivated silicon (H-Si) substrates [24]. Spun cast PS films (approximately 50 nm in thickness) prepared from toluene (Sigma-Aldrich, ACS reagent, >99.5%) solutions [23] were annealed at 150 °C for 48 h in an oil-free vacuum below 10^{-3} Torr to promote adsorption [14] and to ensure equilibrium [15]. The films were then solvent leached a minimum of 5 times (each leach was for approximately 10 min) in baths of fresh toluene at room temperature [25]. The residual layers were dried in a vacuum oven to remove any excess solvent trapped in the films and characterized at room temperature by using AutoEL-II ellipsometry (Rudolf Research) [23]. Furthermore, high temperature XR experiments at the X10B beam line of the National Synchrotron Light Source, Brookhaven National Laboratory, were performed under vacuum by using a custom-built vacuum furnace with Kapton windows. The specular reflectivity was measured as a function of the scattering vector in the perpendicular direction, $q_z = (4\pi \sin\theta)/\lambda$, where θ is the incident angle and λ is the x-ray wavelength ($\lambda = 0.087$ nm, which is equivalent to the x-ray energy of 14.2 keV). The XR data were fitted by using a standard multilayer fitting routine for a dispersion value (δ in the x-ray refractive index) in conjunction with a Fourier method, a powerful tool to obtain detailed structures for low x-ray contrast polymer multilayers [26,27]. Note that δ is proportional to the density of a film [28] and the δ value of the bulk PS is $\delta_{\text{bulk}} = 1.14 \times 10^{-6}$. To ensure the equilibrium of the layers at given temperatures, we stabilized for 1 h prior to XR measurements. Details of the neutron reflectivity experiments are described in Supplementary Material [28].

Figure 1 shows a representative time growth curve of the adsorbed PS ($M_w = 170$ kDa) layer thickness (h) measured by ellipsometry. Napolitano and Wübbenhorst introduced a new criterion to define the equilibrium of polymer chain conformations prepared on solid substrates via the ratio t^* between the annealing time and the adsorption time [14]. The adsorption time (τ_{ad}) was estimated to be $\tau_{\text{ad}} \sim 0.6$ h based on the best fit of the proposed function ($h \sim \alpha(1 - \exp[-t/\tau_{\text{ad}}])$: α is a constant) to the experimental growth curve. Therefore the ratio t^* is determined to be $48h/0.6h = 80$ such that our annealing condition has met the criterion for equilibrium identified as $t^* \gg 1$ [14]. We found that the τ_{ad} values for all the adsorbed layers with different M_w are less than 24 h. We also confirmed that the equilibrium adsorbed PS layers are relatively smooth and homogenous, free of noticeable voids or defects based on scanning probe microscopy experiments (data not shown). Moreover, the equilibrium thickness (h_{eq}) of the adsorbed layers at $t^* \gg 1$ showed a linear relationship with the radius of polymer gyration (R_g) [28], reflecting random-walk statistics of polymer chains [8,10]. The observed relationship of $h_{\text{eq}} = 0.78R_g$ ($R_g = \sqrt{N/6} \times a$, where N and a are the degree of polymerization and segment length, respectively) is in good agreement with the previous results for the PS adsorbed layers onto H-Si substrates [10]. Hence, the present results demonstrate that we have achieved equilibrium melts against the solid surface and effectively revealed the adsorbed structures by vitrification of the polymer and subsequent "quick" rinsing (when compared with the prolonged desorption experiments to be discussed later) with the good solvent.

Figure 2 shows a representative XR profile for the equilibrium adsorbed PS ($M_w = 123$ kDa) layer (circles). The XR and the corresponding Fourier transformation (FT) were

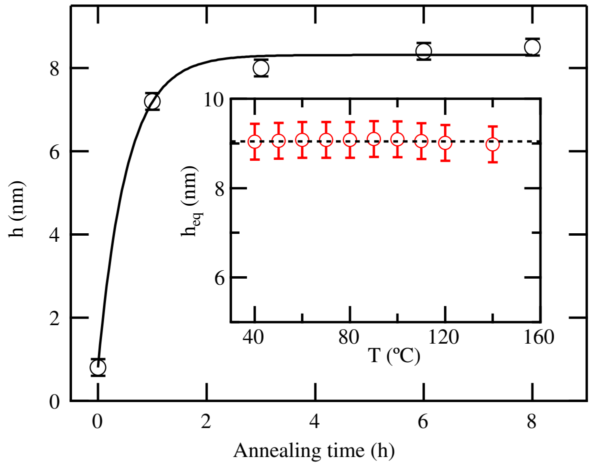

FIG. 1 (color online). Time evolution of the adsorbed PS ($M_w = 170$ kDa) layer thickness during annealing at 150 °C. The solid line corresponds to the proposed function described in the text. In the inset, the temperature dependence of the thickness of the equilibrium adsorbed PS ($M_w = 170$ kDa) layer is shown.

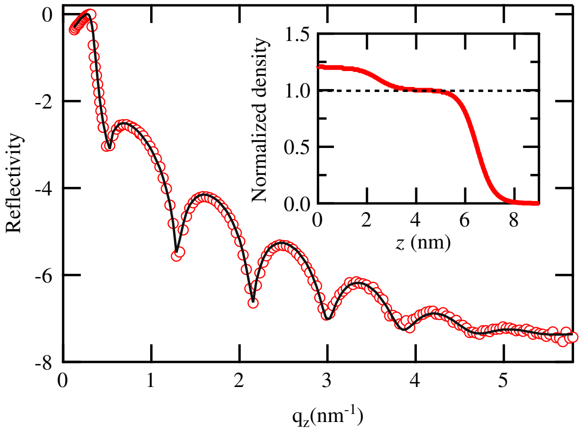

FIG. 2 (color online). Observed XR profiles for the equilibrium adsorbed PS (M_w = 123 kDa) layer (circles). The solid line corresponds to the best fit based on the density profile against the distance (z) from the SiO_2 surface shown in the inset. The dispersion values were converted into the density of the film relative to the bulk by using the measured dispersion value of the bulk.

fit simultaneously using a dispersion model [28]. Based upon the FT profile [28], a four layer model (silicon substrate, native oxide, and two different density PS layers) was chosen. The thickness of the SiO_2 layer was determined to be about 1.0 nm from a XR measurement on a bare H-Si substrate. The best fit (the solid line in Fig. 2) could be obtained with the density profile of the two polymer layers shown in the inset. The best-fitting results gave us the thickness of 2.8 ± 0.2 nm and δ of $(1.4 \pm 0.1) \times 10^{-6}$ for the bottom PS layer next to the SiO_2 layer, while δ of the top layer (4.4 ± 0.2 nm in thickness) remains bulklike ($\delta = 1.14 \times 10^{-6}$). Moreover, we found that all the adsorbed layers with different M_w show similar architectures composed of the nearly identical inner higher density region [$\delta = (1.4 \pm 0.1) \times 10^{-6}$ and 2.8 ± 0.5 nm in thickness] regardless of M_w and the outer bulklike density region whose thickness increases with increasing M_w [28].

It is interesting to address that the XR results are reminiscent of the picture developed by Granick and coworkers for polymer adsorption from a dilute solution: polymer molecules arriving first on the surface are adsorbed with a flat conformation, while late arriving ones, which find fewer free surface areas, adsorb more loosely with fewer adsorbed sites [19–22]. In fact, Napolitano and Wübbenhorst pointed out that polymer adsorption from the melts can also be explained by the same concept, while they have not clarified the inner architectures of the adsorbed layers [14]. It is therefore reasonable to suppose that the early arriving polymer chains lie flat on the substrate, forming the inner high-density region, and the late coming chains adsorb loosely onto the substrate, developing the outer bulklike density region (the inset of Fig. 3). As shown in the inset of Fig. 1, we also found that h_{eq} remains nearly constant with increasing temperature up to 150 °C, which is consistent with the previous results on the adsorbed PS layer using capacitive dilatometry [11]. Thus, it is clear that the outer loosely adsorbed polymer chains have the nearly zero thermal expansion.

Next, we reveal the inherent architecture of the flattened chains. For this purpose, it is desirable to uncover the inner high-density region by preferentially removing the outer bulklike density region. This was successfully achieved by utilizing the large difference in the desorption energy, which is proportional to the number of segment-surface contacts, between the outer loosely adsorbed chains and the flattened chains [29,30]. We immersed the equilibrium adsorbed layers in a bath of fresh toluene at room temperature for up to 5 months. Note that the experiments were carried out in the continually replenished solvent to facilitate the desorption kinetics [31]. The resultant layers after the given desorption times were dried in a vacuum oven to remove any excess solvent and then characterized by using XR. Figure 3 shows representative desorption kinetics for the adsorbed PS layer (M_w = 170 kDa). From the figure we can see that the thickness of the adsorbed layer decreases with increasing desorption time and reaches the final thickness of 3.5 ± 0.2 nm after 120 days. The XR results demonstrate that the thickness of the final desorbed layer is in good agreement with that of the inner high-density region of the equilibrium adsorbed layer before the desorption experiments [28]. Therefore, we conclude that the prolonged desorption process enables us to unveil the flattened high-density region.

We further provide new insight into the equilibrium conformations of the flattened chains. Figure 4 shows (a) representative XR curves for the lone flattened high-density layer (M_w = 290 kDa) and (b) the temperature dependence of the thickness (h_{flat}) that corresponds to the loop size of the flattened chains, as schematically shown in the inset. Hence it is clear that h_{flat} decreases with

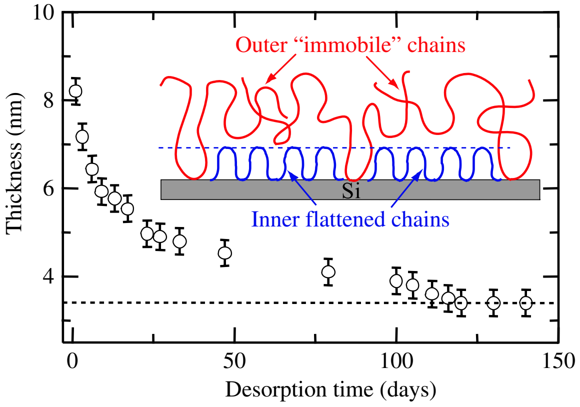

FIG. 3 (color online). Desorption kinetics of the equilibrium adsorbed PS (M_w = 170 kDa) layer during the toluene leaching. The inset shows the schematic view of the two different chain conformations.

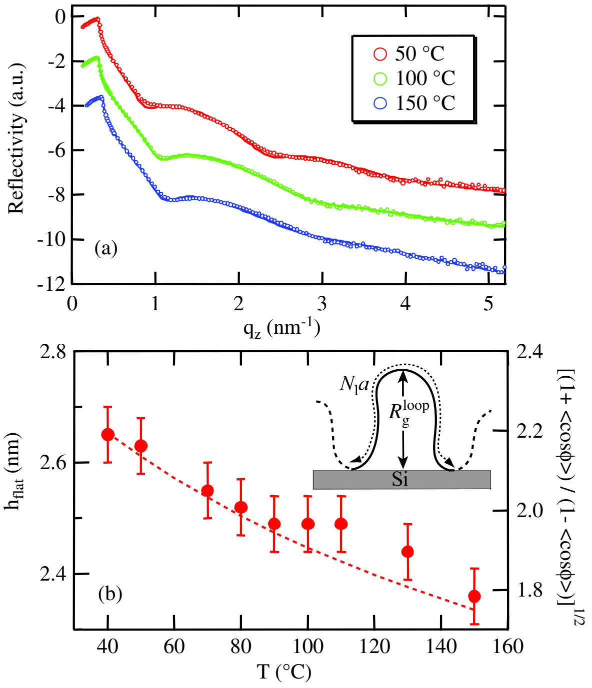

FIG. 4 (color online). (a) Representative XR profiles for the flattened layer ($M_w = 290$ kDa) at the three temperatures [the data correspond (from the top) to 50, 100, and 150 °C, respectively] and (b) temperature dependence of h_{flat} along with the calculated values of the $[(1 + \langle\cos\phi\rangle)/(1 - \langle\cos\phi\rangle)]^{1/2}$ term in Eq. (1) (the dotted line) for PS. The inset shows the schematic conformation of the flattened chains.

increasing temperature up to 150 °C, and we confirmed that the temperature dependence of h_{flat} is reversible. This film contraction is in sharp contrast to the nearly zero thermal expansion of the flattened chains in the equilibrium adsorbed layer before the desorption experiments and could be explained by the resultant empty spaces (i.e., more free volume) after removing the outer loosely adsorbed polymer chains. Density variations of the flattened layer may be difficult to determine for XR owing to the macroscopic textured structures of the flattened layer [28]. Instead, NR, which is a more sensitive technique for determining density change of polymer thin films if one uses deuterated polystyrene (d-PS), was used. Our NR investigations for the d-PS ($M_w = 676$ kDa, $M_w/M_n = 1.15$, Polymer Source) flattened layer reveal film contraction and the corresponding increase in the density of the flattened polymer chains upon contraction: The scattering length density values of the flattened polymer chains are estimated to be $(7.4 \pm 0.1) \times 10^{-4}$ nm^{-2} at 25 °C and $(7.8 \pm 0.1) \times 10^{-4}$ nm^{-2} at 130 °C, respectively, both of which are larger than the scattering length density value of bulk d-PS (6.0×10^{-4} nm^{-2}) [28]. Hence, the important conclusion that the high temperature conditions further densify the flattened chains in equilibrium is drawn. A series of subsequent XR experiments have reproduced the same temperature dependence of h_{flat} with different M_w [28]. Using the self-consistent field theory, Schuetjens and Fleer [4] have shown that the average loop size of isolated long polymer chains (with $N \geq 50$) adsorbed on an attractive surface does not depend on chain length. To our best knowledge, this is the first experimental evidence to validate the generality of the equilibrium chain conformations at the solid-polymer melt interfaces regardless of chain length. However, it should also be emphasized that the theory cannot explain the densification of the loop.

To understand the origin of the densification process occurring within a few nanometers in space, we focus on the local conformations of a polymer chain. For this purpose, we assume that each loop of the flattened chains is composed of N_l segments with backbone bond angles all equal to θ [the inset of Fig. 4(b)] and that the temperature dependence of R_g of the loop (R_g^{loop}) is given in the same way as the bulk [32],

$$R_g^{\mathrm{loop}} = \left[N_l a^2 \frac{(1-\cos\theta)(1+\langle\cos\phi\rangle)}{(1+\cos\theta)(1-\langle\cos\phi\rangle)}\right]^{1/2}, \tag{1}$$

$$\langle\cos\phi\rangle = \frac{1-\exp(-\Delta E/k_B T)}{1+2\exp(-\Delta E/k_B T)}, \tag{2}$$

where ΔE is the energy gap between two conformational states (i.e., *trans* and *gauche* states) and k_B is the Boltzmann constant. From Eq. (1), it is clear that the temperature dependence of R_g^{loop} is directed by the term $(1 + \langle\cos\phi\rangle)/(1 - \langle\cos\phi\rangle)$. Figure 4(b) also plots the calculated values of $[(1 + \langle\cos\phi\rangle)/(1 - \langle\cos\phi\rangle)]^{1/2}$ (the dotted line) with the literature value of $\Delta E = 5.0$ kJ/mol for PS [33]. Although this is a crude approximation without considerations of the effects of excluded volume and surface-segment interactions on the conformations of the flattened chains, we can see the reasonable correlation between h_{flat} and $[(1 + \langle\cos\phi\rangle)/(1 - \langle\cos\phi\rangle)]^{1/2}$ as a function of temperature. We hence postulate that the increase in the fraction of *gauche* conformers at high temperatures [34], which has not been considered in the theory [3–6], leads to the more collapsed conformations of the flattened chains [35]. Further experiments are in progress to seek the generality of the equilibrium conformations of the flattened chains with various surface-segment interactions and intramolecular architectures.

In summary, we have revealed that polymer adsorption from the melts originates in piecemeal deposition with differential spreading dictated by the still-uncovered surface area, as for polymer adsorption from a dilute solution [19–22]. The piecemeal deposition results in the two different chain conformations at the SPM interface regardless of chain length, as opposed to the prevailing view [1] that chain conformations are selected such that free energy is minimized. We also found that the additional prolonged (~120 days) solvent leaching allows us to expose the flattened high-density region to the air interface. Moreover, the *in situ* x-ray and neutron reflectivity measurements elucidate the reversible densification process of the flattened chains at higher temperatures irrespective of chain length. By generalizing the chain conformations of bulks, we postulate that the local conformations (i.e., *trans* and *gauche* states) of a polymer chain play a vital role in this unusual densification process. It is known that polymer adsorption occurs at a nanoparticle (curvature) surface filled in polymer melts as well [36–38] and the adsorbed layer is reported to be significantly thinner around nanoparticle surfaces than at chemically similar flat substrate surfaces [39]. We are currently working on the geometric effects on the architectures of flexible polymer chains, ultimately leading to a better understanding of the thermodynamics at the SPM interfaces.

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